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(54) Title: MULTI-MODAL ANALYSIS OF MICROMECHANICAL STRUCTURES FOR SENSING APPLICATIONS

(57) Abstract: A device and method for determining concentrations of species in an environment using a mechanical resonator. The method employs one or more microcantilever structures where several mechanical mode resonances are determined for the structure during the measurement and used to determine environmental changes around the device or measure alterations in fundamental dimensions or material properties of the structure/material overlayer deposited on the structure.

TITLE OF THE INVENTION

MULTI-MODAL ANALYSIS OF MICROMECHANICAL STRUCTURES FOR SENSING APPLICATIONS

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

The U.S. Government has rights in this invention pursuant to contract number DE-AC05-00OR22725 between the Department of Energy and UT-Battelle, LLC.

FIELD OF THE INVENTION

This invention relates to improved methods and apparatus for detecting and quantifying physical forces and chemical entities using micromechanical structures. More specifically, the invention is directed to the use of not only the fundamental resonance of the mechanical structure for sensing but also combining this signal with one or more higher order mechanical resonances to enhance the sensitivity (signaltonoise ratio). Furthermore, such a technique/apparatus may be used to determine various film properties of deposited structures on surfaces.

BACKGROUND OF THE INVENTION

Cantilevered structures using metallic materials were developed by Taylor in the mid-1970's for various gaseous sensing detectors [Taylor and Waggener, The Journal of Physical Chemistry 83, 1361 (1975)]. Atomic force microscopes use a microfabricated beam structure as a stylus, based on the work of Binnig et al. [Phys. Rev. Lett. 56 930 (1986)]. Sensors for various chemical, physical and biological species also have been described [Thundat et al., Appl. Phys. Lett. 64, 2894 (1994); Thundat et al, Microscale Thermophysical Engineering 1, 185 (1995) and Gimzewski et al. Chem. Phys. Lett., 217, 589 (1994)], all using detection means based on a laser-deflected signal from the stylus to a photodetector.

Several methods to improve sensitivity recently have been explored. In US Patent No. 5,445,008, Wachter et al. teach micromechanical sensing that uses the frequency shift associated with a micromechanical structure's fundamental resonance mode.

In U.S. Patent 5,719,324, Thundat et al. teach the use of fundamental as well as second and third order mechanical resonances of a cantilever structure. This is achieved only through selective deposition of coating materials at particular locations on the structure. Each of the resulting coating schemes creates a different set of structural resonance characteristics. Species to be measured then interact at sites on the structure's mechanical nodes as determined by the selective coating scheme. The method requires a complicated selective coating and is not feasible for routine production at this time. Furthermore, such a coating scheme would work only for a specific mechanical mode of the resonating structure.

Higher sensitivity at a low cost is still a need in many potential detection applications.

SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to provide a sensor that uses an oscillating mechanical beam to not only excite higher mechanical modes of the sensor to enhance its capability but to use these mechanical modes together to further enhance the sensitivity of the device.

It is a further object of the present invention to provide a method of gravimetrically measuring various substances with increased sensitivity.

It is a further object of the present invention to provide a method of selectively sensing chemical vapors and gravimetrically sensing added mass with enhanced signal-to-noise ratios of the mechanical system and to enhance sensor response.

It is a further object of the present invention to provide a means of interrogating film deposition processes so as to allow for detailed understanding of various deposited thin layers on surfaces.

It is a further object of the present invention to provide highly automated electronic readout of the mechanical structure response to facilitate the development of low-cost, high-performance measurement systems for general applications.

These and other objects are achieved in one aspect of the present invention by a device and a method for analyzing changes in micromechanical structure response. The disclosed device utilizes the multi-resonant character of mechanical oscillators to enhance sensor response by simultaneously monitoring the location, in frequency, of one or more of the mechanical resonance modes and correlating the signal against the concentration of the detectable species in the appropriate space. The method requires the identification of the shifts in frequency for different modes or overtones of the fundamental frequency. By utilizing frequency shift methods (i.e.: frequency mixing) to fold higher order mechanical mode resonances into a lower frequency band, it is possible to improve signal-to-noise ratios even when available detectors are operating at their limits of detection.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic view of a piezoelectric transducer and mechanical resonator sensing apparatus before end loading of the mass to be sensed.

Figure 2 is a schematic view of the piezoelectric transducer and mechanical resonator apparatus illustrated in Figure 1 after end loading the mass.

Figure 3 is a schematic representation of the system used to control and monitor multi-mode sensor response.

Figure 4 is a graph of theoretical frequency shift as related to increased resonance mode, based on gravimetric measurements using the apparatus illustrated in Figure 1.

Figure 5 is a graph of mass induced frequency shifts vs. deposited mass for modes 1 through 8.

Figure 6 is a graph the relative sensitivity to mass induced frequency shifts at various modes using experimental data illustrated in Figure 4.

Figure 7 is a semi-log plot of an experimental versus theoretical comparison of the end-loaded sensitivity (gravimetric) of a silicon beam structure. Squares are experimental and circles are theoretical points.

Figure 8 is a simplified graph illustrating frequency shifts and separations as the mode number is increased.

Figure 9 is graph of frequency shifts resulting from deposition of a thin gold (Au) film on a silicon (Si) cantilever bar.

Figure 10 is a plot of frequency fluctuation vs. time over a two-minute interval.

Figure 11 is a block diagram showing a basic detector circuitry for monitoring the cantilever resonance response.

Figure 12 is a block diagram of a dual-channel compensation scheme for monitoring the cantilever resonance response.

Figure 13 is a block diagram of a dual-channel mixing compensation scheme for monitoring the cantilever resonance response.

Figure 14 is a block diagram of an instrument system according to this invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, it has been found that a multi-modal analysis of cantilever structures may be used to improve physical, chemical and biological sensing. This is generally accomplished by measuring the fundamental frequency in conjunction with a number of higher order modes of the mechanical structure and monitoring changes or shifts in these responses upon exposure to selected species to be detected in the environment of the detector. The present invention provides a method and apparatus to dramatically enhance the sensitivity of these measurements to such mass or stress changes by using higher-order modes in particular.

Possible applications are numerous. For example, besides the environmental sensing/monitoring direction, this technology can be applied in the determination of mechanical properties of either deposits upon structures or the structures themselves. From the mathematical relations discussed *infra*, an ability to determine such quantities as modulus of elasticity and precise measures of thickness are also possible. Furthermore, the type of measurement scheme disclosed herein can be extended to vacuum (low-pressure) measurements, which offer the additional bonus of dramatically higher quality factors which in turn will increase the sensitivity of these resonators significantly. Since the present invention provides enhanced knowledge of the dynamic character of a resonator based upon the relative changes of different modal resonances, it can further be used with a

micro-centrifugal separator system by allowing differentiation between aerosols based on their mass as they distribute along the length of the resonator structure.

An additional use is process characterization of coating methods and structural uniformity for micromechanical systems. In time, more emphasis will be placed on the development of coating technologies at the micron scale as applied to microelectromechanical systems (MEMS). With this, a need will exist to interrogate the uniformity of coatings upon these small structures. One scheme will use cantilevered structures placed in a variety of locations along a wafer followed by monitoring the changes in modal resonance as a coating or processing step is performed. A related scheme will involve observation of the uniformity of the coating over one resonator structure and monitor relative changes in modal resonance character of this individual structure.

The method of this invention may be useful in theoretical studies directed to a better understanding of the physical properties of cantilevers and coated cantilevers. Higher order resonances are useful for determining the density, mechanical dimensions and Youngs's modulus for fabricated structures. Such determinations may be used for quality control to determine structure thickness and length and the thickness of an applied coating.

Microcantilevers are typically made of materials such as silicon and silicon nitride, as well as fabricated ceramic, high performance ceramic, or other ceramic specifically composed of a number of substances and combinations of substances, including but not limited to elements of group 14 (IUPAC IVB, CAS IVA) and groups 13/15 (IUPAC IIIB, CAS IIIA/VB,VA). Though other methods exist, the oscillation of these structures is normally induced through the use of a piezoelectric transducer. While oscillating, these structures, also referred to *inter alia* as beams, resonators, cantilevers, microcantilevers, mechanical resonators, micromechanical resonators, mechanical beams, oscillating bars, and resonating microbars, are susceptible to changes (or shifts) in oscillation frequency (or resonance) brought on by effective changes in their geometry and/or structural characteristics or outside forces. The microcantilever may respond to pressure (e.g. light, particles, etc) or changes induced by particles. Coated microcantilevers may respond to selective adsorption of gasses and particles or reactions or other physical interaction modalities. The presence or occurrence of each of these on cantilevers or on an active site of these structures thereby results in a signal response in the form of shifts in oscillation (or resonance) frequency. Changes in frequency are then commonly detected by constant photodiode detection of laser emission reflected off of the resonating structures. One such scheme of detection set-up is found in U.S. Patent 5,719,324, issued to Thundat et al. and hereby incorporated by reference.

Unlike related cantilever sensing methods which measure one mode of resonance (the fundamental mode), the present invention involves the combined analysis of one or more higher resonance-mode frequencies, that is, the simultaneous observation and combined

consideration of multiple resonance-mode frequency shifts. Alternatively, the present invention also comprehends the acquisition of multi-modal frequency shifts at different times but under the same stress or signal conditions, under the assumption that these frequency shifts remains relatively stable over time.

As shown in research related to the present invention, it is possible to observe frequency changes of cantilever structures with a moderate level of sensitivity. See, for example, the theoretical discussions of sensor response, T. Thundat, P.I. Oden and R.J. Warmack, *Microscale Thermophysical Engineering*, 1, pp. 185-199 (1997), hereby incorporated by reference.

By contrast, the present invention considers several higher modes of oscillation up to and including an excitation frequency around 2.8 MHz, the current limit of commercially available sensors. Theoretically, the measurements could be made at even higher frequencies. It is shown by experimental results as well as theoretical discussions that not only are the gravimetric sensitivities of these higher modes of excitation reproducible, but they also produce larger resonance shifts, resulting in greater resolution and, hence, a dramatically more sensitive device. Figure 1 is a schematic representation of device 1, a microcantilever 3 mounted on a piezoelectric (PZT) device 5. Cantilever 3 has a thickness t, a Young's modulus E and a density P. Figure 2 is an illustration of the device of Figure 1 having an additional mass 7 deposited at the distal region of the bar. Under these conditions, the new thickness is t*, the Young's Modulus is E* and the density P*.

Figure 3 is a schematic representation of the system used to control and monitor multi-mode sensor response. The sensor of Figure 1, with a suitable coating (Fig. 2), is caused to vibrate by the PZT device. The vibration is detected using a laser and a photodetector to monitor the vibration. Collectively they are shown as 11. A modal response processing system 13 interfaces the detector to a data acquisition system 15 and is used to seek frequencies on the basis of projected locations or by manual tuning or by use of a software searching sequence.

To understand the method disclosed, it is necessary to consider the properties of a mechanical beam oscillator. Considering a simple beam structure with uniform cross-sectional area, the expression relating modal resonance characteristics is given by:

$$f_n = \frac{\kappa_n^2 t}{2\pi\sqrt{12}}\sqrt{\frac{E}{\rho}} \qquad (1)$$

where n is the specific mode of oscillation, and t, E, are the respective thickness, Young's modulus of elasticity and density of the structure. The symbol is a quantity dependent upon the geometry of the resonator and is determined by solving the equation:

$$\cos(\kappa L)\cosh(\kappa L) + 1 = 0 \tag{2}$$

This is for successive values of , where L is the length of the resonator bar. Upon solving, values of are given by: 1,875, 4.694, 7.855... for n= 1, 2, 3... This method was utilized to advance from one resonance mode of the mechanical structures to the next.

$$\kappa_n L = \xi_n = 1.875, 4.694, 7.855, 10.996, 14.137, \ldots, \frac{2n-1}{2}\pi \tag{3}$$

Then equation (1) may be written:

$$f_n = \frac{\xi_n^2}{2\pi\sqrt{12}} \frac{t}{L^2} \sqrt{\frac{E}{\rho}} \tag{4}$$

The utility of this equation is readily apparent. In all acoustic wave sensors (of which the microcantilevered structure are a subset), sensing is accomplished by monitoring changes in response frequency of the device. These changes are induced either by alterations in the material properties of the device, such as through mass addition for gravimetric sensing (e.g. Fig. 2) or exposure to chemical processes on the structure's active area, or through changes in the geometry of the active surface area.

Thus, considering equation (4), it is seen that upon sensing, there are typically three dominant paths for changing the material properties of the structure: first, through alterations in the effective thickness of the structure t; second, through changes in the term through chemical interactions and mass sorption processes on the active surface of the sensor; and third, through alterations in the length of the structure. It should be noted that the only variation in the functional form from mode-to-mode comes through changes of the prefactor.

Furthermore, as higher modes are investigated, such alterations in the cantilevered structure are amplified by an amount proportional to the mode squared. This is illustrated in Figure 4.

This same relationship is also seen in other data, as illustrated in Figure 5. This data shows the sensitivity enhancement obtainable by operating at higher-order resonance modes of a simple beam resonator sensor with mass being deposited upon the last 10 per cent of the length of the structure. In this case, higher order modes are significantly more sensitive (in terms of change in frequency versus added mass) than lower ones, as indicated by the larger slopes. The plot shows mass induced frequency shift (Δ HZ) versus deposited mass in picograms. The mechanical mode n, operating frequency HZ and mass sensitivities are shown at the right. Figure 6 shows tabulation of the data from Figure 5 into the same form as presented in Figure 4. It is clearly seen here that there is a quadratic relationship between the modal frequency shift as compared with the fundamental mode resonance versus mode of excitation.

Additional theoretical discussion related to the sensitivity argument substantiates experimental results and provides insight into the potential performance possibilities of the detection scheme of the present invention. Haener, *Journal of Applied Mechanics*, 25, p. 412 (1958) provided an expression relating the modal resonance of a mechanical structure to end-loaded conditions with various mass amounts. He was able to express the various resonance modes, f_n, in terms of the various mass parameters as:

$$f_n = \frac{1}{2\pi}\sqrt{\frac{EI}{L^3 M_1}\left(\frac{R_n^4}{\frac{M_2}{M_1}\mu_n + k_n} + r_n^4\right)} \tag{5}$$

where I is the cross-sectional moment of inertia, M_1 and M_2 are the total mass of the beam and deposited mass on the end of the structure, respectively. Furthermore, the remaining constants are determined from the characteristic equation for this beam structure as:

$$R_n = \begin{cases} 1.875 & n=1 \\ 4.694 & n=2 \\ \pi(n-1/2) & n>2 \end{cases} \qquad r_n = \begin{cases} 0 & n=1 \\ 3.940 & n=2 \\ \pi(n-3/4) & n>2 \end{cases}$$

$$k_n = \begin{cases} 1 & n=1 \\ 1.9839 & n=2 \\ [1-\{(4n-3)/(4n-2)\}^4]^{-1} & n>2 \end{cases} \qquad \mu_n = \begin{cases} 4.091 & n=1 \\ 21.608 & n=2 \\ 4n(n+0.6) & n>2 \end{cases} \tag{6}$$

Applying this expression to the specific formula and actual data shown in Figures 4 and 5, a close agreement is obtained. (Fig. 6 & 7) In Figure 7, the squares indicate experimental results; the circles conform to theoretical calculations.

At the heart of the present invention is the acquisition and combination of information from one or more of the higher order modes to interpret signal response and correlate the analysis to various sensing applications. Often in a real world mechanical oscillator system, it is observed that there are a substantial number of spurious resonance peaks that are either associated with mechanical coupling of the oscillator to the excitation stage or attributable to other complicated modal patterns of the oscillator (such as torsional motions, etc.) With this in mind, it is necessary to begin with the measured fundamental resonance of the structure and through theoretical mechanics calculations, project the location (in frequency) of the subsequent modes. (Equations 3 and 4) This type of scheme has been used to measure several mechanical resonance modes of structures and can be easily incorporated into a programmable form to monitor these peaks. However, because the exact location of the resonance peaks will not be known, it is necessary to utilize a "frequency-seek" scheme to search for either peaks in the resonance amplitude or the cross-over point in the phase response of the drive compared with the output response.

It should be mentioned that the conditions resulting in collective frequency shifts of these mechanical modes is controlled by several factors. These include variations in the loading geometry of the resonator (i.e. through the placement of the selective chemical coating upon the sensing device) and through the mechanical properties of the overlayer compared to that of the underlying substrate (resonator surface). As an example, a resonance frequency increase on a totally coated mechanical resonator has been observed for certain added species on the device while when other species are added to the same structure, a decrease in the resonance frequency is observed. This last effect is dependent upon the mechanical properties of both the overlayer and the underlying resonating sensor and the form of chemical interaction between surface and analyte. Figure 8 illustrates this phenomenon in a plot of amplitude (arbitrary units) H versus frequency.

The aforementioned shifts at higher modes can be understood in terms of the gravimetric sensitivity S_m:

$$S_m = \lim_{\Delta M \to 0} \frac{A}{f} \frac{\Delta f}{\Delta M} \tag{7}$$

Where A is the active sensing area of the device, f is the resonance frequency and ıs the change in mass on the active sensor area. If is expressed in terms of the density and thickness of the deposit, the general form becomes:

$$S_m^{(n)} = \lim_{\Delta M \to 0} \frac{A}{f^{(n)}} \frac{\Delta f^{(n)}}{\Delta M} = \frac{1}{\rho f^{(n)}} \frac{df^{(n)}}{dt} \qquad (8)$$

When this equation is normalized to area per oscillation frequency (note that the frequency is in the denominator), S_m becomes the definition of the sensitivity of the device. Typical sensitivities of prior art devices are in the range of 10 cm^2/gm to 200 cm^2/ gm. With this method/device, sensitivities in the range of 2000-3000 cm^2/gm have been observed.

We have found that although the equations discussed above are true for all forms of acoustical wave sensors, one advantage to using this method is that it may be optimized to specific detection needs. The sensitivity of a microcantilever is a function of its geometry. The observed shifts are determined by the property of the coating used and its location on the cantilever. Finally, the form of interaction between the coating and the entity being detected will shift the frequency being detected.

Multiple or arrayed sensors may be used to detect different entities in the same sample by using different coatings. Alternatively, two or more different coatings might be applied to the same microcantilever.

Examples of suitable coatings are numerous. Metals, especially noble metals, may be applied by sputtering. Coatings may be applied by microsyringe, brush, Q-tip®, spin casting, dipping, air-brush spraying, Langmuir-Blodgett film transfer, plasma deposition, evaporation, sublimation and self-assembled monolayers as described in U.S. patent 5,445,008. Biosensors may be attached by the methods disclosed in Bastiaans, U.S. patent 4,735,906 or Nakagawa, U.S. patent 5,363,697.

In theory, there is no particular limit to the mode number which is measured. As a practical matter, the limitations result from the photodetector head electronics.

One variation of this concept is to use a frequency shift method (i.e.: frequency mixing) to fold higher-order mechanical mode resonances into a lower frequency band so as to enhance the signal-to-noise ratio for the device and therefore, enhance the sensitivity. In such manner, the errors inherent in measurements of higher frequencies can be minimized

The present invention enables not only acquisition of a signal from a single mode of response, but rather a system which provides a collective measure of many mechanical modes which in turn greatly enhances obtainable knowledge about a mechanical system as applied to sensing. Comparison of the shifts observed for each mode enables one to study the effects of changes in composition of the cantilever and of changes in coatings. Each sensor can be calibrated at the highest detectable mode even though used at a lower frequency. Used as such, the present invention quite surprisingly provides for dramatically superior sensitivity in the detection of barometric pressure (including very high vacuum) and analytes such as mercury vapor, hydrogen, chemical and biological warfare agents and other airborne entities for which early detection of parts-per-billion to parts-per-trillion amounts is considered critical.

The following examples illustrate the use of the invention but are not limiting thereof.

Examples

Two different types of bar-shaped cantilever beams were utilized. The first was composed of polycrystalline silicon, with minimal dimensions of 397 μm, 29 μm, 2 μm (length, width, thickness) provided by Park Scientific Instruments, Inc. (Sunnyvale, CA) and used in force-constant calibrations of force-microscopy cantilever scanning styli. The second structure is a silicon nitride (SiN_x) structure with nominal dimensions of 200 μm, 20 μm, 0.6 μm (length, width, thickness), commercially available for force-microscopy applications from Digital Instruments, Inc. (Santa Barbara, CA). To obtain a modal analysis of cantilevered beams, a standard laser-deflection apparatus with an integrated piezoelectric stage (PZT) for exciting the beam structure into resonance was used (Digital Instruments Nanoscope III Multi-mode laser-deflection head). A Hewlett-Packard model HP3589A network/spectrum analyzer was used to provide the drive signal-to-response measurements using the split-segment photodetector signal. Mechanical-resonance amplitude and phase responses were then exported to a computer for further processing.

The fundamental and several higher mode resonances for the beams were measured by exciting the structure through PZT crystal with a 0.5-V_{RMS} sinusoidal signal and monitoring the amplitude and phase signal through the resonance point.

The cantilever holder assemblies then were transferred to a turbomolecular-pump-driven high-vacuum system with an integrated electro-beam evaporation system. The beams were masked with a glass cover slip to expose only the extreme end to deposition in order to limit the measurement to mass-deposition processes only. Deposition of a thin gold film through the shadow mask was performed in a 5 x 10^{-5} Torr vacuum at a rate of 0.05-0.1 nm/sec.

After removal from the chamber, the deposition area was determined by optical microscopy. In the case of the silicon bar, the area was 1.26 x 10^{-9} m^2 (11% of total structural area); for the SiN_x structures, 6.3 x 10^{-10} m^2 (or 16% area).

The assembly was returned to the laser-deflection head and the frequency-resonance shifts measured. The deposition process and shift measurements were repeated to demonstrate the results for additional masses. A typical result is shown in Fig. 9 and the results for the Si sequence shown is Fig. 5. The experimental vs. theoretical results are compared in Fig. 7.

Frequency-stability measurements ultimately determine a minimum-detectable mass (MDM) or mass density (MDMD) that the sensor can deliver. Therefore, to illustrate the full potential of the present invention, it was necessary to investigate the stability with which frequency measurements can be made for the different modes of oscillation.

Frequency stability was used along with the mass sensitivity of each mode to determine a minimum-detectable mass or mass density. The results of Figure 10 show the typical frequency fluctuation observed for these structures. Specifically, it shows the eighth-mode resonance of the 2 μm thick silicon structure. In all measures of the frequency stability made in the two- or four- minute time scale, a stability in the center frequency within 0.1 to 0.4 Hz was observed through all the observed resonance modes (as determined by the nominal one-standard-deviation spread). This, taken together with the enhanced mass sensitivity of the higher resonance modes, shows that these higher modes exhibit an inherently greater gravimetric sensitivity. As also illustrated in Figure 9, the standard deviation of the signal is 0.179 Hz. Using three standard deviations as an acceptable confidence limit, the minimum detectable mass density for this mode is shown to be 0.57 ng/cm^3, which equates to a minimum detectable mass of 7.2 fg for this test structure, or one part in 7.46 (10^6 when compared to the total mass of the cantilever. Applying the same analysis to the corresponding data for the ninth mode of the SiN_x structure yielded a standard deviation of 0.256 Hz around the center frequency, which represents a minimum-detectable mass density of 0.35 ng/cm^2. This equates to a minimum-detectable mass of 2.2 fg on the sensor (one part in 13.38 (10^6 when compared to the entire cantilever). It is thus seen that the present invention provides a method of gravimetrically sensing mass on the order of femtograms.

In addition to the above mechanical sensing considerations, it should be emphasized that to produce a practical measurement device, the mechanical structure response must be appropriately converted to electrical signals which can be amplified or otherwise conditioned (e.g., filtered, frequency-shifted, or analyzed) by more-or-less conventional means, such as analog, digital, or mixed-mode integrated circuit (IC) devices. In most cases, the electronic subsystem will be incorporated into a custom application-specific integrated-circuit (ASIC) chip for higher production levels. Several block diagrams follow which illustrate typical electronic readout and signal-processing functions required to augment the mechanical

components described above to implement a fully practical measurement system employing the higher-order mode sensing concepts.

A block diagram of a basic readout circuit is shown in Figure 11 below. Here, the fundamental sensing mechanism for cantilever 21 is that of resonance-frequency locking, through a phase-locked loop (PLL) topology which samples the drive 23 and microsensor signals 25, compares their respective phases in the Phase Detector block 29, filters the error voltage in the Nonlinear Integrator 31, and applies the smoothed adjustment signal to the control input of the Sine VCO (voltage-controlled oscillator) 33, which generates the variable-frequency/phase sinusoidal drive signal to excite the mechanical structure (e.g., cantilever). The diagram indicates the availability of both 0° and 90° phases of the drive signal from the VCO; this configuration is often useful for optimum phase-detector performance and affords tightest and most accurate PLL locking (and sensor reading), particularly in low signal-to-noise conditions. Several advanced composite phase-detector circuits can be employed here to accomplish these goals in an inexpensive ASIC format.

The next two drawings (Figures 12 and 13) provide the signal flows for differential measurement topologies which can further enhance the effective accuracy, repeatability, and stability of the basic mechanical-structure sensing scheme. In Figure 12, two identical, proximally mounted sensor devices one being coated (41) and one reference uncoated (43) are deployed with identical PLL drive/readout electronic channels 45a and 45b. It is assumed here that Sensor#1 is the primary measurement device and is coated to sense the selected species or other parameter of interest. It resonates at a nominal frequency f_1. The matching Sensor #2 is completely identical, except that it is ***not*** coated; it operates at f_2. The outputs of both readout circuits are sent to a frequency comparator 47, which calculates the absolute value of the difference-frequency, $|f_1-f_2|$. This offset value represents the change in the mechanical resonance (presumedly at any one or more of the higher-order modes) due to the desired parameter only; at least to a first order, the common-mode effects of pressure, temperature, vibration, power-supply voltage, time, etc. which affect both devices equally will be canceled out. Similarly, in Figure 13 the two output-frequency signals (either sinusoidal or squarewaves) are multiplied (mixed) together at 51 to produce sum- and difference-frequency signals at f_1 , f_2. The following low-pass filter removes the sum component and leaves the difference-frequency ($f=f_1-f_2$). In this form of measurement, the overall signal-to-noise ratio is improved due to the lower equivalent noise-bandwidth of the low-pass filtered output signal. An alternative setup would add a third, stable but adjustable source at f_3 which could be similarly used to downconvert (be mixed with) the main measurement frequency f_1. Often, this third source would be generated by a crystal-controlled, user-programmable frequency synthesizer for greatest application flexibility.

Finally, Figure 14 provides a suggested block-level diagram of a complete measurement system based on the present technology. Here, the main frequency-control (PLL) loop includes a low-noise composite phase detector, a following nonlinear integrator/low-pass filter to smooth the loop error voltage, and one or more sine-wave VCO modules, and an output-drive power amplifier to excite the cantilever (or other mechanical structure used for sensing). Note that with multiple drive oscillators, dual- or multiple-frequency drive schemes are possible; in many cases, these more complex configurations can provide higher sensitivities, lower drift, better interspecies selectivity, and other measurement improvements over the current-art single-frequency excitation methods. Many of these features will be enhanced by the measurement of various intermodulation-frequency (IM) components generated during multifrequency drive conditions by nonlinear mechanical-structure effects either in the sensor or its coating; these data are retrieved in the block labeled "Auxiliary/IMD Detectors" at the lower right. The precise frequencies to be sought can be programmed into the Synthesizer block by the user to facilitate the search for these usually low-amplitude components. As previously mentioned, the magnitudes of these nonlinearities can also be of significant benefit in the characterization of coatings, coating processes, and other effects such as cantilever material fatigue, cracks, or general (e.g., motional) nonlinearities. General operator interface and data-manipulation tasks are handled by an onboard microcomputer; a precision clock frequency/time reference improves measurement accuracy and minimizes drifts. Key operational features of this basic configuration include:

– Automatic sensor mode-order selection easily accomplished;

– Autoranging of sensor using modes (e.g., fundamental for widest dynamic range, highest modes for highest sensitivity);

– Main mode steady-state AC drive (sinusoidal usually); single- or multiple-frequency drive selectable (e.g., for IM measurements);

– Ability to generate and analyze transient drive/readout waveforms (e.g., pulse, wavelet);

– Attainable accuracies up to 1 part in 10^{10}, plus noise;

– Circuitry easily integrated into standard mixed-mode CMOS format;

– Multichannel architecture ideal for ASIC implementation;

– Ability to store ensembles of mode-frequency sets as a signature (including amplitudes);

– Capability to add sum/difference frequency synthesis for synchronous IM distortion measurements (for extreme sensitivity);

– IM measurements could be used to continually assess cantilever/mechanical system health (via appearance of nonlinearities);

– Processing to permit tradeoffs of noise bandwidths vs. speed of measurement;

– Ability to perform internal calibrations, temperature/drift compensation, etc.

The following is a key to Figure 14:

61: mode selector

63: precision clock

65: counter

67: display (e.g. CRT)

69: synthesizer

71: frequency controller

73: low noise phase detector

75: auxiliary IM detector with programmable lock-in circuit

77: readout

It will be understood that various details of the invention may be changed without departing from the scope of the invention. Furthermore, the foregoing section description is for the purpose of illustration only, and not for the purpose of limitation.

CLAIMS

We claim:

1. A method for determining the concentration of an analyte in a gaseous sample comprising:

coating a microcantilever with a material interactive with an analyte;

inducing a vibration in said microcantilever;

measuring the frequency of vibration of the microcantilever at one or more accessible mechanical resonances;

calibrating said microcantilever by introducing known concentrations of analyte to the microcantilever;

measuring the vibrational frequencies at one or more accessible modes for each concentration;

introducing an unknown concentration of analyte to the microcantilever;

measuring the vibrational frequencies at one or more accessible modes;

determining the concentration of analyte by comparison of the observed frequency shifts.

2. A method according to Claim 1 wherein the determination of the concentration of analyte is made by comparison of the frequency shift of the highest accessible mode.

3. A method according to Claim 1, wherein the measurement of the frequency of vibration is made by comparing the frequency to a reference frequency signal.

4. A detector for the measurement of a physical property comprising a microcantilever beam or other mechanical structure excited to the nth mode of vibration and means for determining the vibrational frequency of at least one mode greater than the first mode.

5. A detector according to Claim 4, wherein the excitation is accomplished by an attached piezoelectric device.

6. A detector according to Claim 4, wherein the physical property measured is temperature/heat.

7. A detector according to Claim 4, wherein the physical property measured is light.

8. A detector according to Claim 4 wherein the physical property measured is mass.

9. A detector according to Claim 4 wherein the physical property measured is an adsorption isotherm.

10. An instrument for monitoring changes in a space comprising multiple detectors according to Claim 4.

11. A method for determining at least one quantity selected from the group consisting of thickness, Young's modulus and density of the structure comprising:

a) determining the modal resonance characteristic defined by the formula:

wherein n is the specific mode of oscillation and t, E, ρ are the respective thickness, Young's modulus of elasticity and density of the structure and k_n is a quantity dependent upon the geometry of the resonator and is determined by solving the equation:

$$f_n = \frac{\kappa_n^2 t}{2\pi\sqrt{12}}\sqrt{\frac{E}{\rho}} \qquad (1)$$

wherein

$$\cos(kl)\cosh(kL)+1=0 \qquad (2)$$

and,

b) calculating the applicable sets of values for t, E and ρ.

12. A method for the detection of the masses of particles in a centrifugal separator comprising measuring the masses of one or more particles distributed along the length of the structure containing a detector according to claim 4.

13. An instrument system incorporating the detector according to Claim 4, including electronic means of generating AC and/or DC detector drive signals and achieving readout of detector output signals at one or more excitation frequencies.

14. The system according to Claim 13, having at least one readout amplifier.

15. The system according to Claim 13, having at least one phase-locked loop to automatically adjust the operating frequency(ies).

16. The system according to Claim 13, having at least one drive amplifier to provide electrical excitation to the mechanical sensing device(s).

17. The system according to Claim 13, having at least one phase/frequency detection means to monitor the operating frequency(ies) and/or phase(s).

18. The system according to Claim 13, having at least one adjustable-frequency oscillator.

19. The system according to Claim 13, having means to adjust the amplitude(s) of the drive-signal(s) used to excite the mechanical sensing device(s).

20. The system according to Claim 13, having interfacing means to couple the drive signal(s) to the mechanical sensing device(s).

21. The system according to Claim 13, having filtering means to low-pass filter the loop frequency/phase error signal(s).

22. The system according to Claim 13, having integrating/averaging means to smooth or shape the loop frequency/phase error signal(s).

23. The system according to Claim 13, having filtering means to smooth or remove noise from the readout signal(s).

24. The system according to Claim 15, further having at least one phase-locked loop with both in-phase and quadrature signal outputs for quadrature (two-phase) drive of the mechanical sensing device(s).

25. The system according to Claim 17, further having at least one frequency/phase detector with more than two inputs.

26. The system according to Claim 17, further comprising multiple cross-coupled phase-detection means.

27. The system according to Claim 17, further comprising multiple inter-coupled phase-detection means.

28. The system according to Claim 17, having at least one digital phase-frequency detector.

29. The system according to Claim 17, having at least one analog (balanced-modulator) phase/frequency detector.

30. The system according to Claim 17, having at least one digital exclusive-OR phase/frequency detector.

31. The system according to Claim 13, further comprising frequency-comparison means for comparing the operating frequencies of at least one mechanical sensing device with either a selected reference frequency or another one or more mechanical sensing device(s).

32. The system according to Claim 31, wherein said frequency-comparison means is a digital counter.

33. The system according to Claim 31, wherein said frequency-comparison means is a microcomputer.

34. The system according to Claim 31, wherein said frequency-comparison means is a dedicated digital logic device.

35. The system according to Claim 31, wherein said frequency-comparison means is a frequency-to-voltage or frequency-to-current converter.

36. The system according to Claim 31, wherein said frequency-comparison means is a downconverter or multiplier or frequency/phase mixer.

37. The system according to Claim 35, further comprising means for filtering the output signal to remove extraneous components.

38. The system according to Claim 36, further comprising means for filtering the output signal to remove extraneous components.

39. The system according to Claim 14, further comprising at least one capacitive-input readout amplifier(s).

40. The system according to Claim 13, further comprising at least one auxiliary detector means to monitor selected intermodulation or harmonic frequencies produced by the mechanical sensing device.

41. The system according to Claim 14, further comprising at least one frequency-source means to provide stable operational frequencies for mechanical device drive and/or readout and/or detection purposes.

42. The system according to Claim 41, wherein at least one of said frequency-source means is a crystal-controlled frequency synthesizer or waveform generator.

43. The system according to Claim 14, having a digital processor or computer means to accomplish system control and/or user-interface functions.

44. The system according to Claim 31, wherein the frequency downconversion means is (are) further used to improve the measurement noise bandwidth(s).

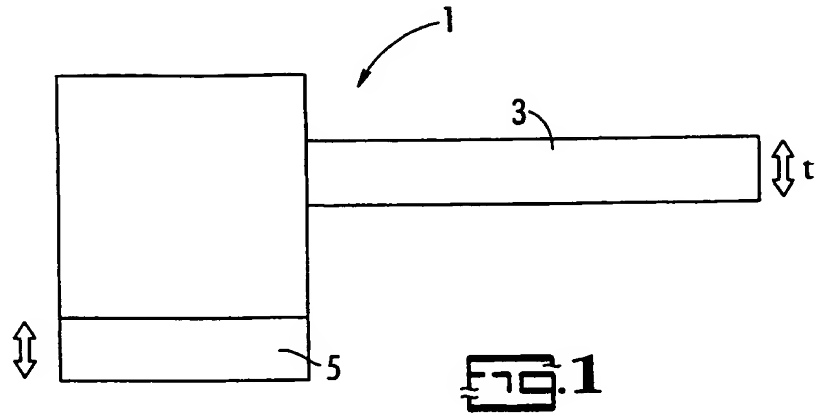

Fig.1

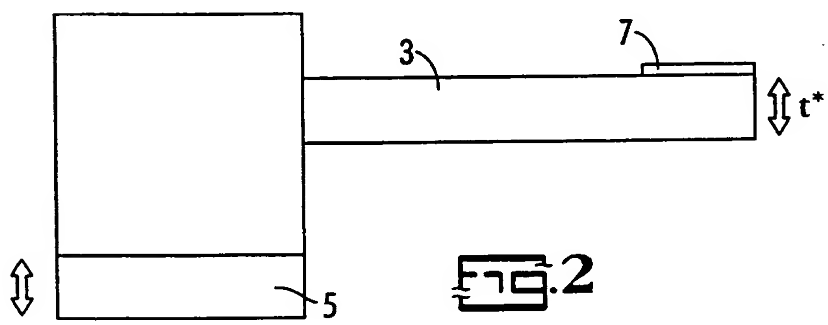

Fig.2

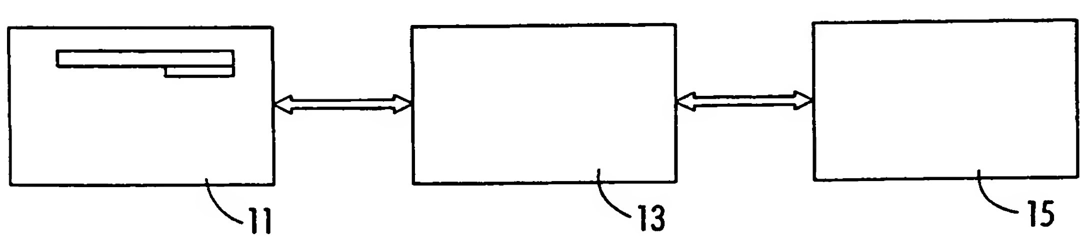

Fig.3

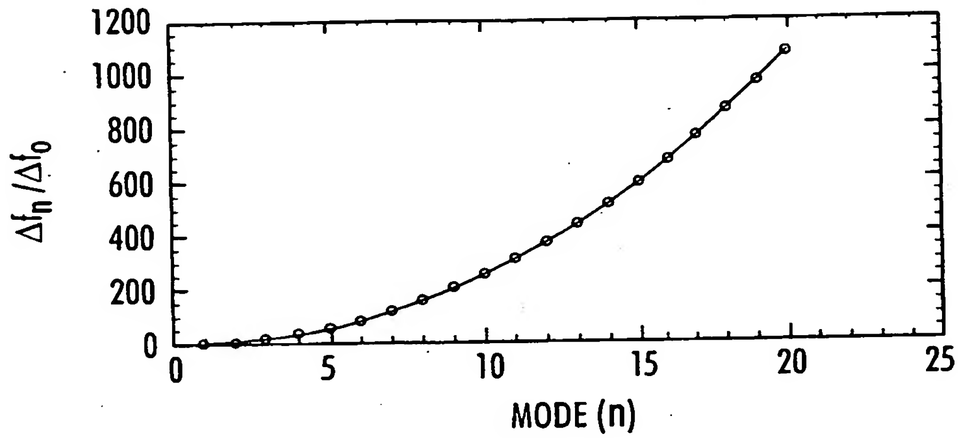
1200
1000
800
600
400
200
0
$\Delta f_n / \Delta f_0$
0
5
10
15
20
25
MODE (n)

FIG. 4

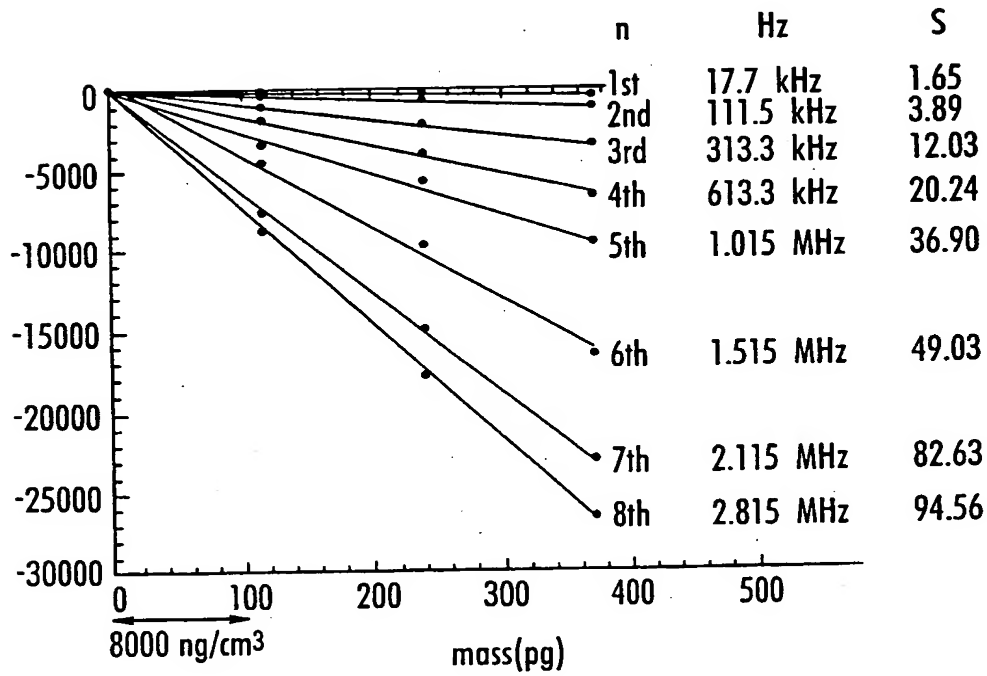
n
Hz
S
1st
17.7 kHz
1.65
2nd
111.5 kHz
3.89
3rd
313.3 kHz
12.03
4th
613.3 kHz
20.24
5th
1.015 MHz
36.90
6th
1.515 MHz
49.03
7th
2.115 MHz
82.63
8th
2.815 MHz
94.56
0
-5000
-10000
-15000
-20000
-25000
-30000
0
100
200
300
400
500
8000 ng/cm3
mass(pg)

FIG. 5

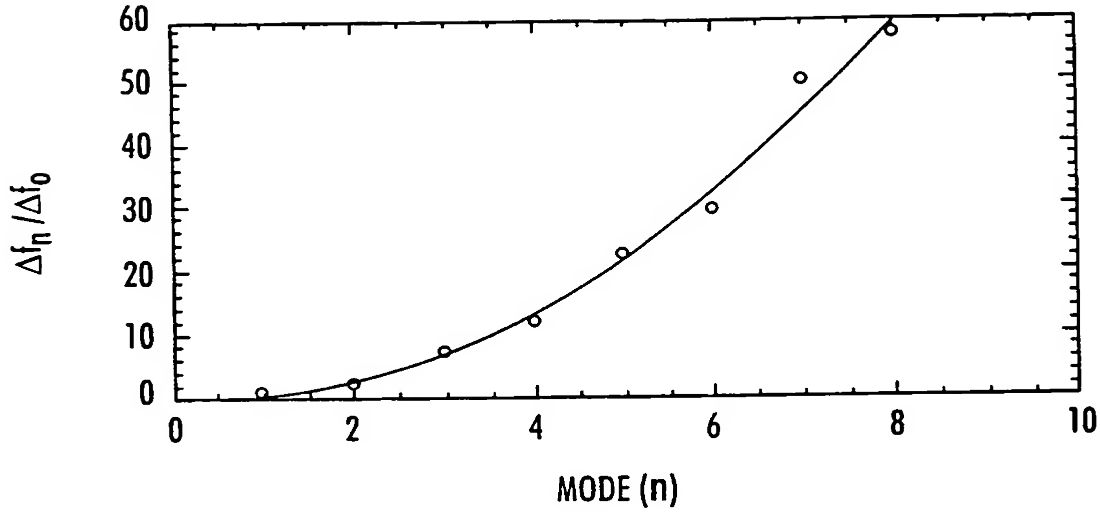
60
50
40
30
20
10
0
$\Delta f_n / \Delta f_0$
0
2
4
6
8
10
MODE (n)

FIG.6

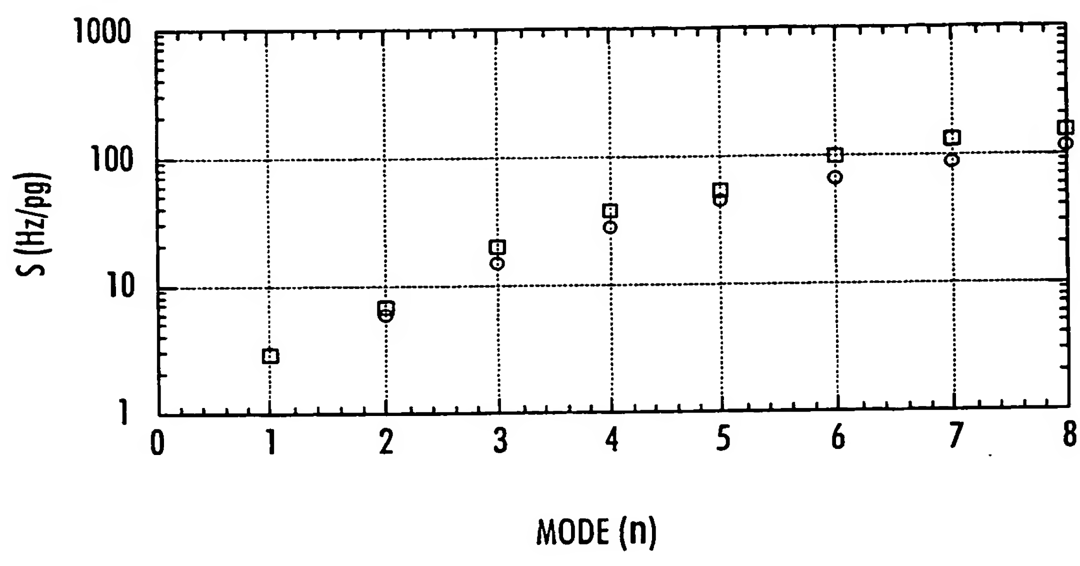
1000
100
10
1
S (Hz/pg)
0
1
2
3
4
5
6
7
8
MODE (n)

FIG.7

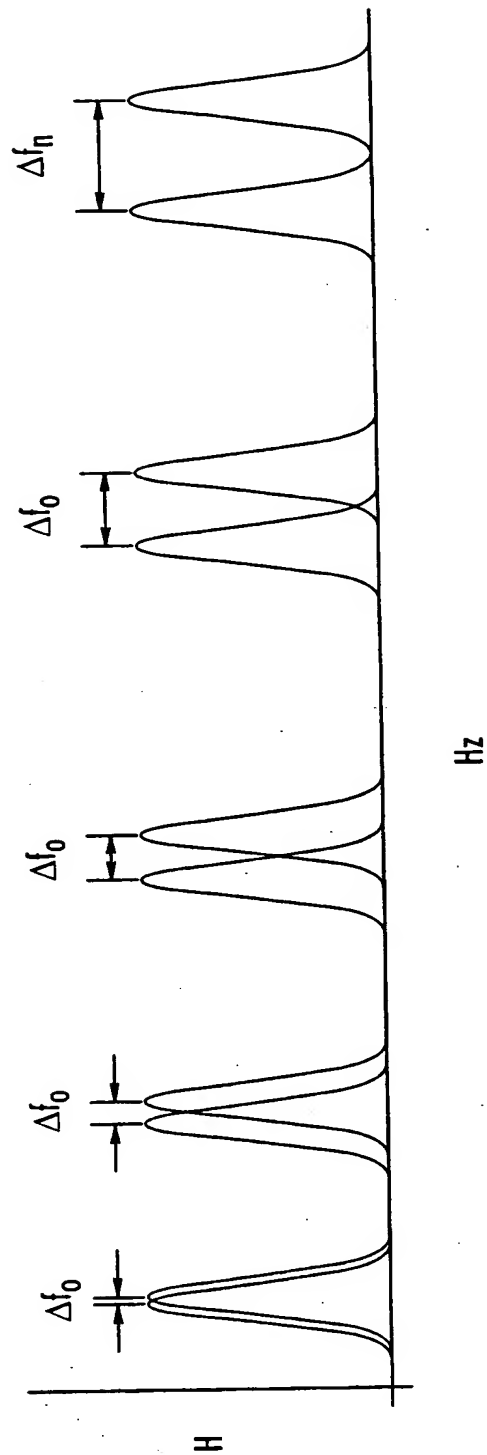

Fig. 8

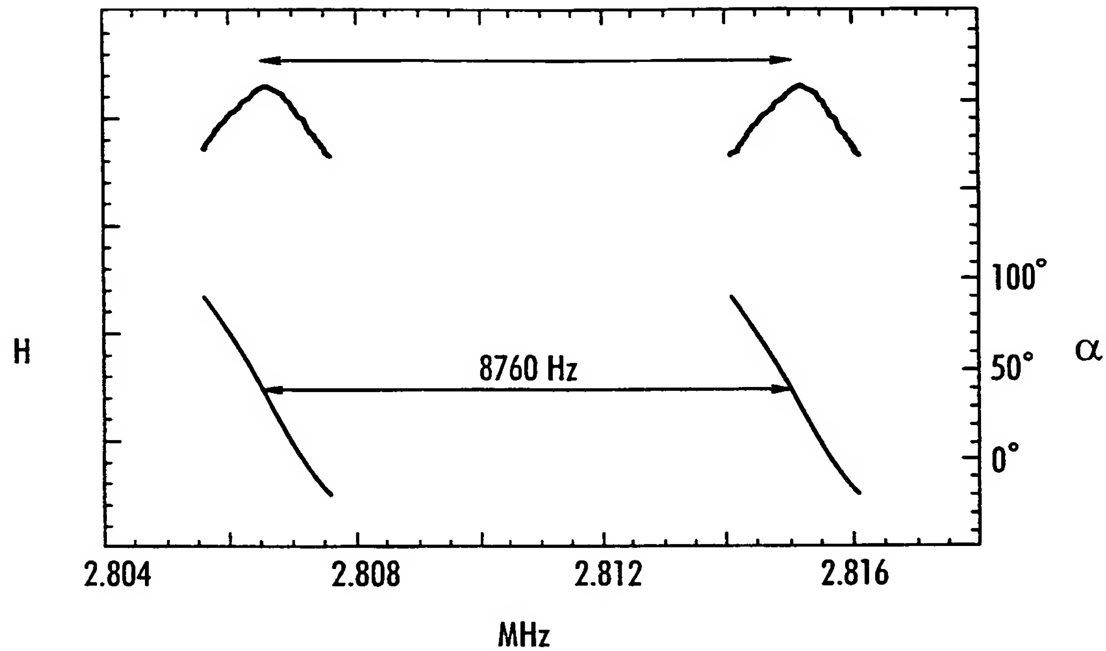
H
100°
50°
0°
α
8760 Hz
2.804
2.808
2.812
2.816
MHz

Fig.9

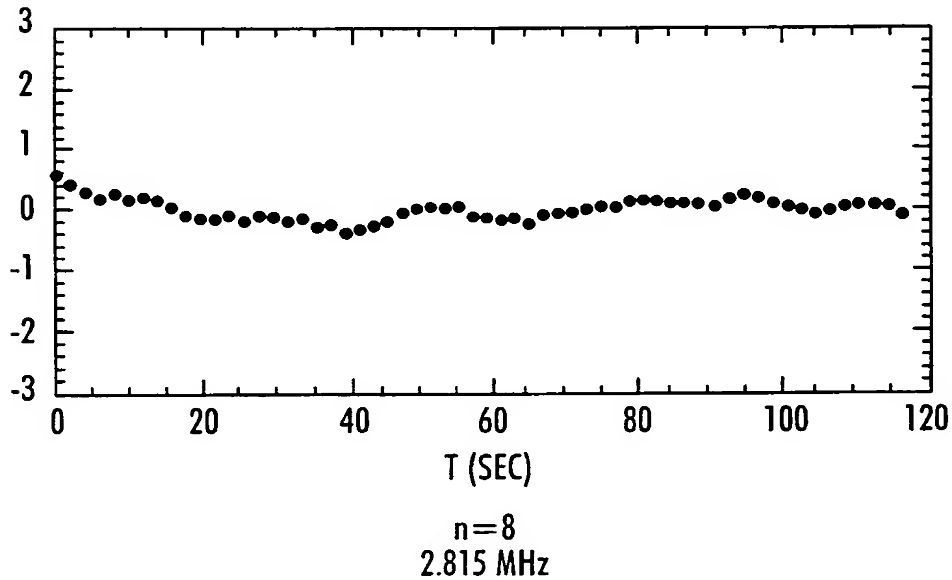
3
2
1
0
-1
-2
-3
0
20
40
60
80
100
120
T (SEC)
n=8
2.815 MHz

Fig.10

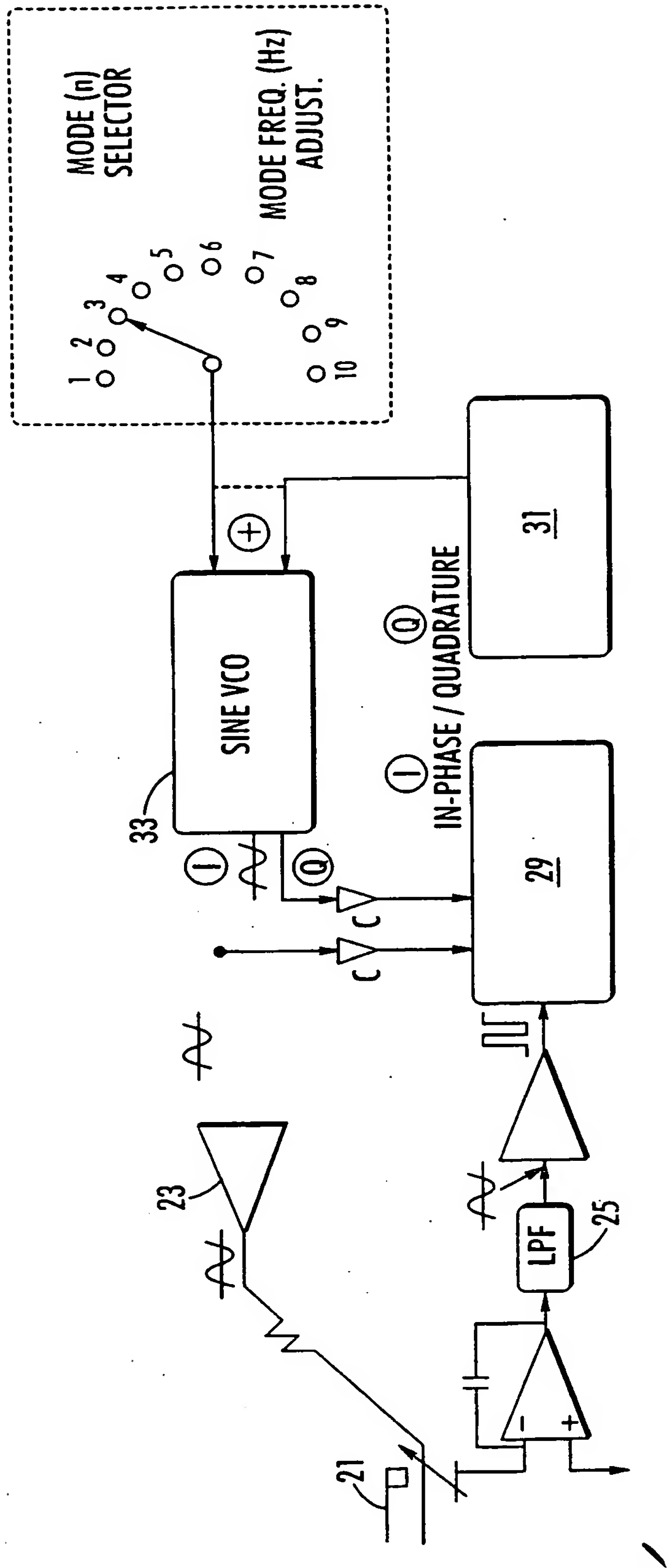
MODE (n) SELECTOR
MODE FREQ. (Hz) ADJUST.
1
2
3
4
5
6
7
8
9
10
+
SINE VCO
33
I
Q
IN-PHASE / QUADRATURE
31
29
C
C
23
LPF
25
21
-
+

Fig. 11

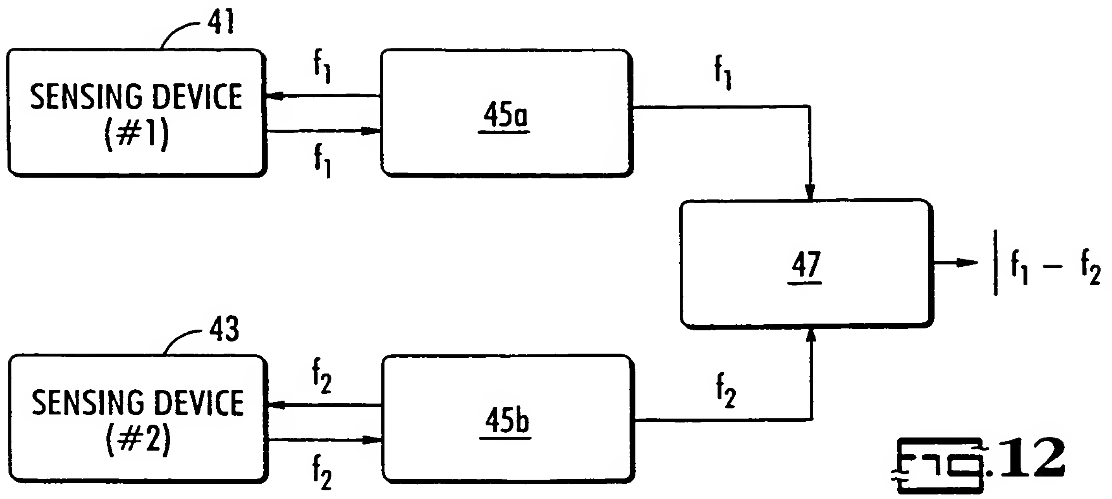
41
SENSING DEVICE
(#1)
f1
f1
45a
f1
47
|f1 − f2|
43
SENSING DEVICE
(#2)
f2
f2
45b
f2

FIG. 12

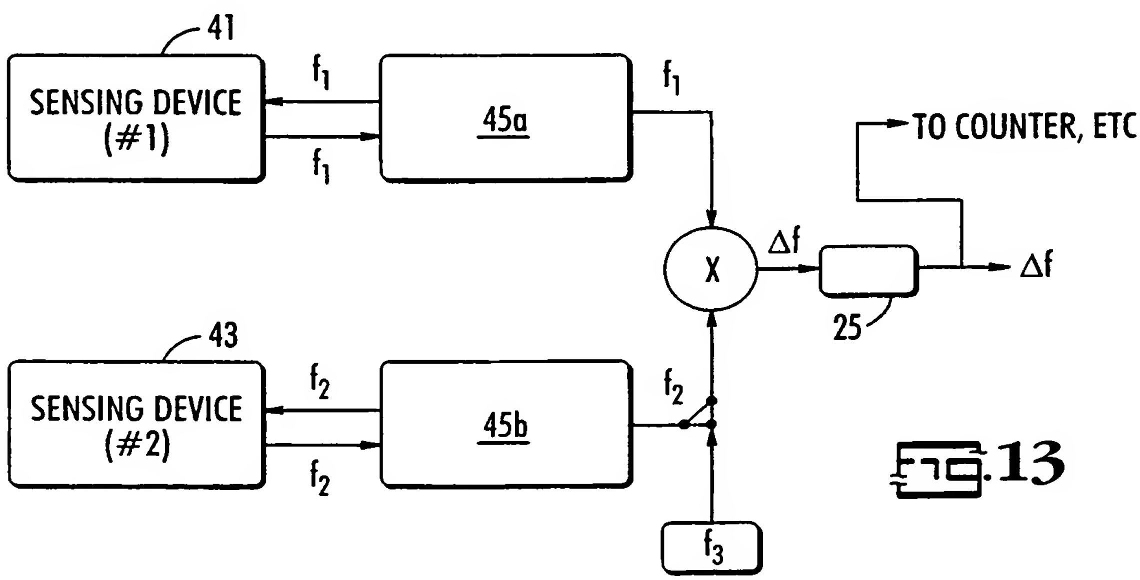
41
SENSING DEVICE
(#1)
f1
f1
45a
f1
X
Δf
TO COUNTER, ETC
Δf
25
43
SENSING DEVICE
(#2)
f2
f2
45b
f2
f3

FIG. 13

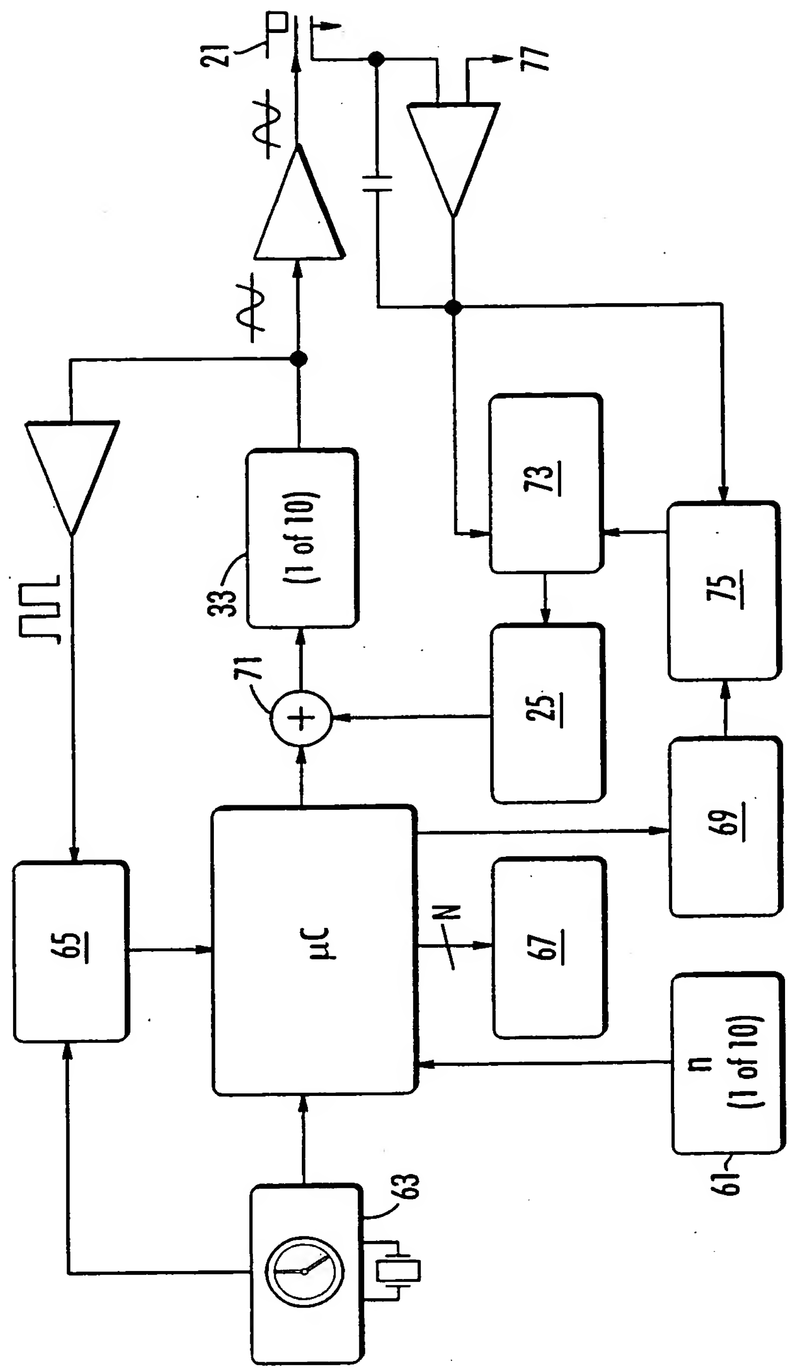

Fig.14

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/17379

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N27/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 072 744 A (BENDIX CORP) 23 February 1983 (1983-02-23) abstract; figure 2	1,4, 10-13
Y	WO 99 30159 A (SENSE Q ;HOEOEK FREDRIK (SE)) 17 June 1999 (1999-06-17) page 6, line 16 -page 8, line 13	1,4, 10-13
A	US 3 540 265 A (LYNNWORTH LAWRENCE C) 17 November 1970 (1970-11-17) column 2, line 4 - line 41	1
X	DE 43 23 045 C (SPECS GES FUER OBERFLAECHENANA) 15 December 1994 (1994-12-15) claim 1	4

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 November 2000	06/12/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Duchatellier, M

1

Form PCT/ISA/210 (second sheet) (July 1992)

Interr nal Application No
PCT/US 00/17379

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 744 902 A (VIG JOHN R) 28 April 1998 (1998-04-28) abstract ---	6,8
A	US 4 947 677 A (FRYE GREGORY C ET AL) 14 August 1990 (1990-08-14) abstract ---	9
A	EP 0 215 669 A (SEIKO INSTR & ELECTRONICS) 25 March 1987 (1987-03-25) abstract; figure 16 ---	10
A	T. THUNDAT: "microcantilever sensors" MICROSCALE THERMOPHYSICAL ENGINEERING, vol. 1, 1997, pages 185-199, XP000900643 cited in the application page 186, paragraph 1 -----	11

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/17379

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0072744	A	23-02-1983	CA	1180914	A	15-01-1985
			DE	3269822	D	17-04-1986
			JP	58039929	A	08-03-1983
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			EP	1034430	A	13-09-2000
			SE	9704354	A	25-05-1999
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US 5744902	A	28-04-1998	NONE			
US 4947677	A	14-08-1990	NONE			
EP 0215669	A	25-03-1987	JP	62207930	A	12-09-1987
			JP	62288546	A	15-12-1987
			JP	62288547	A	15-12-1987
			JP	62064934	A	24-03-1987
			JP	63011835	A	19-01-1988
			US	4789804	A	06-12-1988